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SELF-DIFFUSION IN UNIFORMLY DEFORMED *A*–(*C*) INTERSTITIAL SOLID SOLUTIONS WITH CUBIC LATTICES

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Diffusion processes in solids are determined finally by interatomic interaction forces. One of the reasons for changing the interatomic interaction energy is crystal deformation. In the present work, the self-diffusion coefficient is calculated for uniformly deformed *A*–(*C*) interstitial solid solutions with BCC and FCC lattices. Calculations are performed for vacancy models of diffusion theory [1, 2]. In this model, the diffusion coefficient is determined as a ratio of flux density j of isotopes of atom A to the corresponding gradient of isotope concentration in the direction i ($i = x, y, z$) $\partial n / \partial i$:

$$D = -\frac{j}{\partial n / \partial i}. \tag{1}$$

It is considered that diffusion by hopping of atom A can proceed only to the nearest vacant site, and the probability of transition per unit time is

$$w = \frac{1}{\tau_0} e^{-\frac{\Delta u}{kT}}, \tag{2}$$

where τ_0 is time on the order of the oscillation period corresponding to the maximum frequency in the acoustic spectrum of the crystal, Δu is the height of the potential barrier separating the central atom and the neighboring vacancy. Designating the concentration of vacancies in the sites by c_v, we can write for the flux of atoms A, for example, in the direction of the Ox axis

$$j_x = -w a_x^2 c_v \frac{\partial n}{\partial x} \tag{3}$$

(where a_x is the lattice constant in the direction of the Ox axis). From here for the diffusion coefficient we obtain

$$D_x = \frac{a_x^2}{\tau_0} c_v e^{-\frac{\Delta u}{kT}}. \tag{4}$$

Thus, the problem is reduced to calculations of c_v and Δu in the deformed *A*–(*C*) crystal.

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Let us consider the crystal with BCC lattice in which interstitial atoms *C* occupy octa-interstices. The deformed state is assigned by the diagonal deformation tensor with components $\varepsilon_1, \varepsilon_2$, and ε_3. Then the lattice constants along the *Ox*, *Oy*, and *Oz* axes are written in the form

$$a_x = a(1+\varepsilon_1), \;\; a_y = a(1+\varepsilon_2), \;\; a_z = a(1+\varepsilon_3), \tag{5}$$

where *a* the lattice constant for the non-deformed crystal. In this case, octa- and tetra-interstices in BCC solutions are split into positions of three types with energies $u_i^{(0)}$ and $u_i^{(T)}$ (i = 1, 2, 3). In FCC crystals, interstices do not split after deformation, only the energies of octa- and tetra-interstices are shifted [3].

The equilibrium vacancy concentration for a preset temperature of the solution can be found from the extremum conditions for free energy *F* of the system [2–4] that allow the vacancy concentration $c_v^{(0)}$ for atoms *C* occupying octa-interstices $c_v^{(0)} = \dfrac{n_v}{N_A}$ to be written in the form

$$c_v^{(0)} = \frac{1}{(1-c_C)^3} \exp\left\{-\frac{1}{kT}\left(\frac{z}{2} v_{AA} - \sum_{i=1}^{3} c_C^{(i)} u_i^{(0)}\right)\right\}. \tag{6}$$

Here c_C is the concentration of atoms *C* occupying octa-interstices in the alloy, $c_C^{(i)}$ is the concentration of atoms *C* occupying interstices of the *i*th type, N_A is the number of central atoms A in the solution, n_v is the number of vacancies, z is the coordination number, and v_{AA} is the energy of the pair $A-A$ taken with the minus sign. Considering that the c_v value is small, we obtain

$$\sum_{i=1}^{3} c_C^{(i)} u_i^{(0)} = 3c_C u^{(0)} + \frac{3c_C}{2} a^2 \left\{\frac{1}{2} j_{AC} \left(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2\right) + j_{AC}^{(1)} \left((\varepsilon_1+\varepsilon_2)^2 + (\varepsilon_1+\varepsilon_3)^2 + (\varepsilon_2+\varepsilon_3)^2\right)\right\}, \tag{7}$$

from which we finally derive

$$c_v^{(0)} = \frac{1}{(1-c_C)^3} e^{-\frac{u^{(0)}}{kT}} \varphi_1(T) \varphi_2^{(0)}(T), \tag{8}$$

where $u^{(0)}$ is the energy of vacancy formation in the solution *A*–(*C*) with atoms *C* occupying octa-interstices,

$$\varphi_1(T) = \exp\left\{\frac{1}{kT}\frac{a^2 j}{12}(\varepsilon_1+\varepsilon_2+\varepsilon_3)^2\right\}, \tag{9}$$

$$\varphi_2^{(0)}(T) = \exp\left\{\frac{3c_C a^2}{2kT}\left[\frac{1}{2} j_{AC}\left(\varepsilon_1^2+\varepsilon_2^2+\varepsilon_3^2\right) + j_{AC}^{(1)}\left((\varepsilon_1+\varepsilon_2)^2 + (\varepsilon_1+\varepsilon_3)^2 + (\varepsilon_2+\varepsilon_3)^2\right)\right]\right\} \tag{10}$$

(here j, j_{AC}, and $j_{AC}^{(1)}$ are positive constants [3]).

If atoms *C* occupy tetra-interstices,

$$c_v^{(T)} = \frac{1}{(1-c_C)^6} e^{-\frac{u^{(T)}}{kT}} \varphi_1(T) \varphi_2^{(T)}(T), \tag{11}$$

where $u^{(T)}$ is the energy of vacancy formation with atoms *C* occupying tetra-interstices and

$$\varphi_2^{(T)}(T) = \exp\left\{\frac{3c_C a^2 j_{AC}}{40kT}\left[(\varepsilon_1+4\varepsilon_2)^2+(\varepsilon_1+4\varepsilon_3)^2+(\varepsilon_2+4\varepsilon_1)^2+(\varepsilon_2+4\varepsilon_3)^2+(\varepsilon_3+4\varepsilon_1)^2+(\varepsilon_3+4\varepsilon_2)^2\right]\right\}. \tag{12}$$

For FCC lattices without interstice energy splitting, the vacancy concentration can also be described by Eqs. (8) and (11) in which $1/(1-c_C)^3$ and $1/(1-c_C)^6$ are substituted by $1/(1-c_C)$ and $1/(1-c_C)^2$ and $\varphi_2^{(0)}$ and $\varphi_2^{(T)}$ are

$$\varphi_2^{(0)}(T) = \exp\left\{\frac{3c_C j_{AC}^{(0)} a^2}{2kT}\left(\varepsilon_1^2+\varepsilon_2^2+\varepsilon_3^2\right)\right\}, \tag{13}$$

$$\varphi_2^{(T)}(T) = \exp\left\{\frac{3c_C j_{AC}^{(T)} a^2}{12kT}\left(\varepsilon_1+\varepsilon_2+\varepsilon_3\right)^2\right\}. \tag{14}$$

In calculations of the diffusion coefficient *D*, we first consider the *A*–(*C*) solution with FCC lattice and atoms *C* occupying octa-interstices.

The height of the diffusion potential barrier is determined by the energy difference between the atom *A* in position *S* neighboring to the vacant site *V* and the saddle point *P* lying in the middle of the segment *S* – *V* [2]:

$$\Delta U = U(P) - U(S), \tag{15}$$

where

$$U(P) = -6v_{AA}^0 - 6c_C v_{AC} + 0.004 j_{AA} a^2 - 0.04 j_{AA} a^2 c_C (\varepsilon_1+\varepsilon_2+\varepsilon_3) + o(\varepsilon^2), \tag{16}$$

$$U(S) = -7v_{AA}^0 - 6c_C (v_{AC} + 2v'_{AC}) + o(\varepsilon^2). \tag{17}$$

Here v_{AA}^0, v_{AC}, and v'_{AC} are energies of *A*–*A* pairs and *A*–*C* pairs with the first and second neighbors taken with the minus sign.

From here, neglecting the terms quadratic in ε_i, we derive

$$\Delta U = v_{AA}^0 + 0.004 j_{AA} a^2 + 12 c_C v'_{AC} - 0.04 j_{AA} a^2 c_C (\varepsilon_1+\varepsilon_2+\varepsilon_3). \tag{18}$$

In the approximation linear in the diffusion tensor components, substituting Eq. (18) into Eq. (4), we finally obtain

$$D_i = \frac{1+2\varepsilon_i}{(1-c_C)^3} \frac{a^2}{\tau_0} e^{-\frac{Q_0+\Delta Q}{kT}}, \tag{19}$$

where $Q_0 = \Delta U_0 + u_v$ (u_v is the energy of vacancy formation in the non-deformed *A*–(*C*) crystal) is the energy of self-diffusion activation in the non-deformed solution and ΔQ is its change after deformation:

$$\Delta Q = a\left(\varepsilon_1 + \varepsilon_2 + \varepsilon_3\right), \quad a = \text{const}. \tag{20}$$

This additive term ΔQ in Eq. (19) is proportional to $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \dfrac{\Delta V}{V}$ – relative change of the volume. Deformation generally leads to small anisotropy *D* (of the order of several percent). We now pay attention to the strong dependence of *D* on the impurity concentration. Thus, *D* increases approximately by 3% for $c_C \approx 0.01$ and by 16% for $c_C \approx 0.05$.

Analogous result are obtained for the *A*–(*C*) solutions with atoms *C* incorporated in tetra-interstices and the only difference that the term $1/\left(1-c_C\right)^6$ with stronger dependence of *D* on the impurity concentration arises in the pre-exponential factor of *D* instead of the term $1/\left(1-c_C\right)^3$.

A more complicated situation is observed for alloys with FCC lattice. The diffusion flux in the direction of the *Ox* axis in this case arises due to transitions of central atoms to the neighboring vacant sites located in planes perpendicular to the *Oz* and *Oy* axes, so that

$$j_x = j_x^{(1)} + j_x^{(2)}. \tag{21}$$

In the first case, considering that atoms *C* occupy octa-interstices, we perform calculations analogous to Eqs. (15)–(18) and obtain that the height of the diffusion potential barrier is

$$\Delta U = 7v_{AA}^0 + 4v_{AC}^0 + \Gamma a^2\left(\varepsilon_1 + \varepsilon_2 + 4\varepsilon_3\right), \tag{22}$$

where

$$\Gamma = 2j_{AA} + c_C j_{AC}. \tag{23}$$

In the second case, the ΔU value differs by substitutions $\varepsilon_2 \to 4\varepsilon_2$ and $4\varepsilon_3 \to \varepsilon_3$.

Calculating fluxes $j_x^{(1)}$ and $j_x^{(2)}$ and considering that ε_i are small, we obtain

$$D_x = \frac{1+2\varepsilon_1}{1-c_C}\frac{a^2}{\tau_0}\exp\left(-\frac{Q_0 + \Delta Q_x}{kT}\right), \tag{24}$$

where

$$\Delta Q_x = \frac{\Gamma a^2}{2}\left(\varepsilon_1 + 5\varepsilon_2 + 5\varepsilon_3\right). \tag{25}$$

Expressions for D_y and D_z are derived from Eq. (24) in which ε_1 in the pre-exponential factor and in ΔQ_x has been replaced by ε_2 and ε_3, respectively.

Thus, unlike the BCC crystals, the anisotropy of not only the pre-exponential factor, but also of the self-diffusion activation energy is observed in FCC solutions. Analogous results are obtained for diffusion in solutions with impurity atoms occupying tetra-interstices; in this case, the factor $1/\left(1-c_C\right)^2$ stands for the factor $1/\left(1-c_C\right)$ in the expression for *D*.

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